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(54) **Process for preparing
filler-containing
polytetrafluoroethylene fine
powder**

(57) A powder of a polymer of tetrafluoroethylene and a filler which is negatively charged in water is prepared by mixing aqueous dispersions of polymer particles and filler particles. The filler particles have polyvalent cations adsorbed on their surfaces so as to be positively charged. The mixing is conducted in the presence of an anionic surfactant and a water immiscible organic liquid. The product coagulates and can be recovered from the resultant dispersion.

SPECIFICATION

Process for preparing filler-containing polytetrafluoroethylene fine powder

5 The present invention relates to a process for preparing filler-containing polytetrafluoroethylene (PTFE) fine powder. More particularly, it relates to a process for preparing filler-containing PTFE fine powder wherein the filler is uniformly dispersed in PTFE without separation.

For production of filler-containing PTFE fine powder, there is known the so-called "coagulation process" wherein the filler in a powdery state is dispersed into an aqueous dispersion of PTFE prepared by emulsion polymerization in an aqueous medium so as to coagulate PTFE together with the filler. The filler-containing PTFE fine powder prepared by this process is used, like PTFE fine powder not containing any filler, for manufacture of a molded product by paste extrusion or by calendaring.

15 In the said coagulation process, there is usually employed a hydrophilic filler. In order to achieve the uniform mixing of such hydrophilic filler with PTFE which is hydrophobic, it is considered to be necessary to make hydrophobic the surfaces of the particles of the filler. In fact, there has been proposed a method for making hydrophobic the surfaces of the particles of the filler by treatment with a polyorganosiloxane or a condensed titanate ester (Japanese Patent Publn. (examined) No. 33253/1972), a cationic surfactant (Japanese Patent Publn. (examined) No. 12052/1973) or a chromium complex salt of a carboxylic acid (Japanese Patent Publn. (examined) No. 37576/1973). As the result, however, the treated filler is lowered in dispersibility into water and more or less coagulated. Thus, the dispersion of the filler at the primary particle level becomes difficult, and the uniform mixing with PTFE is sometimes prevented.

20 The basic object of the present invention is to provide a filler-containing PTFE fine powder wherein the particles of PTFE and of the filler are uniformly mixed and separation of the particles of the filler therefrom does not occur. This object is attained by mixing together an aqueous dispersion of the particles of PTFE and an aqueous dispersion of the particles of a filler, which can be charged negatively in water, adsorbed with polyvalent cation at the surfaces of the particles to be charged positively in the presence of an anionic surfactant and a water-immiscible organic liquid to coagulate the particles of PTFE and of the filler in combination, followed by recovering the coagulated particles from the dispersion mixture.

25 By the above process, the uniform mixing of the hydrophobic PTFE particles and the hydrophilic filler particles can be attained with ease. This reason is still uncertain but may be considered as follows: the filler particles charged in negative adsorb polyvalent cation at the surfaces so as to be charged positively; the anion of the hydrophilic group in the anionic surfactant is adsorbed onto the positively charged surfaces of the filler particles whereby the filler particles are covered by the hydrophobic group bonding to the hydrophilic group; and the hydrophobic group is

previously bonded to the PTFE particles or, even if not, has an affinity to the PTFE particles so that the surfaces of the filler particles are bound with the PTFE particles.

30 In the process of this invention, PTFE may be a homopolymer of tetrafluoroethylene or a copolymer of tetrafluoroethylene with any other polymerizable monomer (e.g. hexafluoropropylene, chlorotrifluoroethylene, perfluoroalkyl vinyl ether) as a modifier in an amount of not more than 2% by weight based on the weight of the copolymer. The aqueous dispersion of the PTFE particles is preferred to contain from 5 to 50% by weight, preferably from 5 to 20% by weight, of the PTFE particles having an average particle size of from about 0.1 to 0.3 μ .

35 As the filler, there may be used any conventional one which is chargeable negatively in water. Specific examples are glass, bronze, zirconium silicate, mica, talc, aluminum oxide, iron oxide, lead oxide, asbestos, cadmium oxide, zirconium oxide, titanium oxide (rutile type), etc. These fillers usually have a particle size of 0.001 to 200 μ . The amount of the filler to be used may be from 5 to 60 % by volume to the volume of PTFE.

40 Whether the particles of the filler are charged positively or negatively in an aqueous medium can be readily confirmed by electrophoresis. For instance, water is admitted in a beaker, and two electrodes which are respectively available as a positive electrode and a negative electrode are dipped therein. An aqueous dispersion of the filler particles is dropped at the intermediary point between the two electrodes, whereby the filler particles charged positively will be precipitated while coming to the negative electrode. If the filler particles are charged negatively, those will be precipitated while coming to the positive electrode. When desired, the charge of the filler may be quantitatively determined by the use of a Tiselius' U-shape tube.

45 As the source of the polyvalent cation to be adsorbed on the surfaces of the filler particles so as to make charged positively, there may be used polyvalent metal salts such as aluminium salts, iron (ferrous and ferric) salts, magnesium salts, calcium salts, barium salts, copper (cupric) salts and zinc salts. Among them, aluminium salts are particularly preferred, because aluminium ion does not leave any coloring in the resulting product. These polyvalent metal salts may be used in the minimum amount for making the filler particles charged positively.

50 A typical procedure for determining such minimum amount is as follows: a determined amount of the filler is admitted in a test tube, and water and a polyvalent metal salt are added thereto, followed by shaking sufficiently; an anionic surfactant and a water-immiscible organic liquid are added thereto, and the resultant mixture is observed on whether the filler is transferred to the organic liquid layer. The amount of the polyvalent metal salt when the entire amount of the filler particles could transfer to the organic liquid layer may be considered as the minimum amount of the polyvalent metal salt to be employed.

55 According to the above procedure using powder of glass fiber (average diameter, 11 μ ; average

length, 80 μ) (10 g) as the filler, aluminium nitrate (Al(NO₃)₃·9H₂O) as the polyvalent metal salt, ammonium perfluorooctanoate (0.01 g) as the anionic surfactant and petroleum benzin (5 ml) as the organic liquid, the relationship of the amount of aluminium nitrate with the transference of the glass

fiber powder to the petroleum benzin layer was determined, and the results are shown in the following table, from which it is understood that the minimum amount of aluminium nitrate is 0.005 g to 10 g of glass fiber powder:

Table 1

Aluminium nitrate (g)	State of glass fiber powder
0	entire powder precipitated
0.0001	partly transferred to the organic liquid layer and partly dispersed in the water layer
0.005	entire powder transferred to the organic liquid layer
0.01	"
0.8	"

Likewise, the relationship of the amount of aluminium nitrate with the transference of red iron oxide powder ("R-110-2" manufactured by Titanium Industry Co., Ltd.) (5 g) used as the filler instead of the glass fiber powder to the petroleum benzin layer

was determined, and the results are shown in the following table, from which it is understood that the minimum amount of aluminium nitrate is 0.005 g to 5 g of red iron oxide powder:

Table 2

Aluminium nitrate (g)	State of red iron oxide powder
0	entire powder precipitated
0.0001	partly dispersed in the water layer
0.005	entire powder transferred to the organic liquid layer
0.01	"
0.1	"

Since the filler itself is hydrophilic, its aqueous dispersion can be readily produced by dispersing the particles of the filler into an aqueous medium (usually water) with the aid of a conventional mixing machine. Addition of the polyvalent cation source such as a polyvalent metal salt to the resultant aqueous dispersion affords an aqueous dispersion comprising the positively charged particles of the filler, which is to be admixed with an aqueous dispersion of PTFE. There may be from 1 to 120 parts by volume of the filler in the aqueous dispersion per 100 parts by volume of the medium.

Mixing of the above-prepared aqueous dispersion of the PTFE particles and the above prepared aqueous dispersion of the positively charged filler parti-

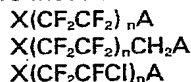
cles may be effected by combining them together, followed by agitation. Usually, the use of any coagulating agent is not required, because the coagulation of the PTFE particles and the filler particles starts immediately after the mixing. The start of the coagulation can be readily detected by the rapid increase of the viscosity of the dispersion mixture, for instance, by the aid of a torque meter equipped on the agitator. After the viscosity reaches the maximum, it is lowered quickly, at which the coagulated particles are precipitated. When the viscosity becomes again constant, the agitation is stopped. The coagulated particles are precipitated or float in the aqueous medium.

In the above mixing operation, the presence of an

anionic surfactant and a water-immiscible organic liquid is essential. Their presence is effective in preventing the separation of the filler particles from the coagulated particles with PTFE and also in making the coagulated particles globular in shape.

The anionic surfactant may be added to the mixture of the aqueous dispersions of the PTFE particles and of the filler particles but is usually previously included in at least one of the aqueous dispersions of the PTFE particles and of the filler particles. In the case that the anionic surfactant is to be included in the aqueous dispersion of the PTFE particles, there may be preferably used the aqueous dispersion of PTFE obtained by emulsion polymerization of tetrafluoroethylene with or without any modifier monomer in an aqueous medium containing an anionic surfactant as the emulsifier. When the aqueous dispersion of PTFE is prepared by the use of a nonionic surfactant as the emulsifier, an anionic surfactant may be incorporated therein. In the case that the anionic surfactant is to be included in the aqueous dispersion of the filler particles, it is added to the aqueous dispersion of the filler after being charged positively.

As the anionic surfactant, there may be used any conventional one such as a higher fatty acid salt, an alkyl sulfate, an alkylaryl sulfate, an alkyl sulfonate, an alkylaryl sulfonate or an alkyl phosphate. Particularly preferred is a fluorine-containing carboxylate or sulfonate anionic surfactant having a perfluoroalkyl or perfluorochloroalkyl group, of which examples are those of the following formulas:



(wherein X is hydrogen, fluorine or chlorine, A is $-COOH$ or $-SO_3H$, or the residue of its alkali metal or ammonium salt and n is an integer of 3 to 10). The amount of the anionic surfactant to be used may be usually from 0.01 to 5% by weight to the weight of PTFE. These fluorine-containing surfactants are sublimated on heating so that they do not remain in the ultimate product.

As the water-immiscible organic liquid, there is preferably used one having a boiling point of 30 to 150°C and a surface tension of not more than 35 dyne/cm. Specific examples are hydrocarbons (e.g. hexane, heptane, gasoline, lamp oil, toluene), chlorinated hydrocarbons (e.g. carbon tetrachloride, trichloroethylene), fluorinated hydrocarbons (e.g. trichlorotrifluoroethane, difluorotetrachloroethane, fluorotrichloromethane), etc. Among them, trichlorotrifluoroethane is particularly preferred. The amount of the water-immiscible organic liquid may be from 30 to 100 parts by weight to 100 parts by weight of the solid components.

Recovery of the coagulated particles from the dispersion mixture is readily accomplished by a conventional separation procedure.

The thus recovered coagulated particles, which have usually an average particle size of 200 to 5000 μ , possess a good flowing property and do not produce any block or lump after drying. Thus, they are easily handled. In fact, they are readily shaped into a sheet, a tube, a stick, etc. by a conventional opera-

tion for paste extrusion or calendering.

As understood from the above, the process of this invention makes it possible to mix the PTFE particles and the filler particles uniformly without separation. It may be noted that filler-containing PTFE fine powder can be obtained by simple continuous operations in a single vessel within a short time. The obtained filler-containing PTFE fine powder can advantageously contain a relatively large amount of the filler and/or have a relatively large specific gravity without separation.

Practical embodiments of the present invention are illustratively shown in the following Examples, wherein part(s) and % are by weight, unless otherwise indicated.

Examples 1-6 and

Comparative Examples 1-7

Into a 5000 ml volume cylindrical vessel of 180 mm in diameter equipped with an anchor type agitator of 80 mm in rotation outer diameter at a distance of 50 mm from the bottom, water (1000 ml) was charged, and powder of glass fiber of 11 μ in average diameter and 80 μ in average length (60 g) was added thereto while agitation. To the resultant mixture, aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) in an amount as shown in Table 3 was added, and an aqueous dispersion of PTFE having a solid content of 25% (960 g) prepared by emulsion polymerization using ammonium perfluorooctanoate as a dispersing agent was added thereto under agitation. The viscosity of the mixture was increased rapidly and reached to the maximum within a period of 15 to 30 seconds. Then, the viscosity dropped down, and after 1 to 5 minutes, a coagulated product started to float. Agitation was further continued for about 5 minutes and stopped.

On the above coagulation, trichlorotrifluoroethane (hereinafter referred to as "F-113") in an amount as shown in Table 3 was added to the mixture in case of Examples at the following stage:

- I: before the start of the increase of the viscosity;
- II: between the maximum of the viscosity and the floating of the coagulated product;
- III: after the floating of the coagulated product.

After the agitation was stopped, the coagulated product was collected by filtration using a metal net of 100 mesh and dried at 120°C. The weight of the glass fiber powder in the filtrate was measured. The apparent density (g/ml) and the average particle size (μ) were measured, and the results are shown in Table 3 wherein aluminium nitrate was not used in Comparative Examples 1 and 7 and F-113 was not used in Comparative Examples 1, 2, 4, 5 and 6.

Table 3

	Aluminium nitrate (g)	F-113		Glass fiber powder separated (g)	Produced powder	
		Stage added	Amount (g)		Apparent density (g/ml)	Average particle size (μ)
Example 1	0.5	II	60	1	0.52	1600
Example 2	2	II	50	1	0.44	1000
Example 3	8	II	100	1	0.71	620
Example 4	2	II	150	1	0.74	650
Example 5	5	III	150	1	0.71	550
Example 6	5	I	150	1	0.79	580
Comparative Example 1	—	—	—	51	—	—
Comparative Example 2	0.1	—	—	52	—	—
Comparative Example 3	0.1	III	75	50	0.49	840
Comparative Example 4	0.5	—	—	38	—	—
Comparative Example 5	2	—	—	41	—	—
Comparative Example 6	8	—	—	47	—	—
Comparative Example 7	—	II	75	49	—	—

The powder (100 parts) obtained in Examples 1, 3, 5, 6 and 8 was admixed with naphtha (16.5 parts), and the resultant paste was extruded with a reduction ratio of 250 and an extrusion speed of 8 mm/minute to give a tube of 5 mm in outer diameter

and 4 mm in inner diameter, which was baked at 380°C for 20 minutes. The tube was subjected to measurement of tensile load at break and elongation according to JIS (Japanese Industrial Standard) K 6892 (1976). The results are shown in Table 4.

Table 4

Powder	Extrusion pressure (kg)	Tensile load at break (kg)	Elongation (%)
Powder of Example 1	3450	9.1	180
Powder of Example 3	3390	8.9	175
Powder of Example 5	3580	8.7	170
Powder of Example 6	3200	9.2	185
Powder of Example 8	3250	9.1	175

Example 7

Glass fiber powder-containing PTFE fine powder was prepared in the same manner as in Example 4 but using 120 g of glass fiber powder and incorporating previously ammonium perfluorooctanoate (1 g) into the aqueous dispersion of PTFE. The glass fiber powder was not substantially contained in water. The apparent density of the obtained powder was

0.76 g/ml, and the average particle size was 620 μ .

20

Example 8

Glass fiber powder-containing PTFE fine powder was prepared in the same manner as in Example 6 but using perchloroethylene as the organic liquid. The obtained powder had an apparent density of 0.75 g/ml and an average particle size of 760 μ .

Example 9

Into the same vessel as in Example 1, water (200 ml) was charged, and glass fiber powder (60 g) and aluminium nitrate (0.06 g) were added thereto, followed by agitation. After addition of ammonium perfluorooctanoate (0.2 g), agitation was effected. To the resulting mixture, petroleum benzin (100 ml) was added, and agitation was carried out, whereby the glass fiber powder was transferred to the petroleum benzin layer and floated therein. The same aqueous dispersion of PTFE as used in Example 1 (1000 ml) was added thereto, and agitation was effected. The resultant mixture was filtered, and the separation of

the glass fiber powder was not observed in the filtrate.

Comparative Example 8

The same procedure as in Example 9 but using no petroleum benzin was effected. In the filtrate, the separation of glass fiber powder (37 g) was observed.

Examples 10-13, Comparative Examples 9-10 and Reference Examples 1-4

The same procedure as in Examples 1 to 6 but using the filler and the polyvalent cation source as shown in Table 5 was carried out. The results are shown in Table 5.

Table 5

	Filler (g)	Polyvalent cation source (g)	F-113		amount of filler separated (g)	Obtained powder	
			Stage added	Amount (g)		Apparent density (g/ml)	Average particle size (μ)
Example 10	Bronze ^{*1)} (300)	Al(NO ₃) ₃ ·9H ₂ O (3)	III	150	1	0.90	490
Example 11	Bronze (300)	AlCl ₃ ·6H ₂ O (2)	II	150	1	0.95	1100
Example 12	Alumina ^{*2)} (300)	AlCl ₃ ·6H ₂ O (3)	II	150	1	0.56	1050
Example 13	Red iron ^{*3)} oxide (50)	AlCl ₃ ·6H ₂ O (2.5)	II	150	1	0.52	1050
Comparative Example 9	Bronze (300)	—	—	—	290	—	—
Comparative Example 10	Bronze (300)	Al(NO ₃) ₃ ·9H ₂ O (6)	—	—	280	—	—
Reference Example 1	Titanium ^{*4)} oxide (15)	—	—	—	1	0.42	400
Reference Example 2	Titanium oxide (15)	—	II	100	1	0.53	810
Reference Example 3	γ -Alumina ^{*5)} (15)	—	—	—	1	0.41	390
Reference Example 4	γ -Alumina (15)	—	II	100	1	0.55	740

Note: *1) Particle size, 350 mesh pass; *2) α -alumina, "Sumitomo Alumina A-21" manufactured by Sumitomo Metal Industries, Ltd.; *3) "R-110-2" manufactured by Titanium Industry, Co., Ltd.; *4) "Titanium dioxide P 25" (anatase type titanium oxide) manufactured by Nihon Aerosil Co., Ltd.; *5) "Aluminum oxide C" manufactured by Nihon Aerosil Co., Ltd.

Titanium oxide and γ -alumina used as the fillers in Reference Examples 1 to 4 are charged positively in water. Thus, they can be admixed uniformly with PTFE particles without cation treatment or coexistence of any organic solvent and are not separated into the filtrate.

As in Examples 1 to 6 but using naphtha in an amount as shown in Table 6, the powder obtained in Example 11 or 13 was subjected to paste extrusion. The extruded product was baked and subjected to measurement of physical properties. The results are shown in Table 6.

Table 6

Powder	Amount of naphtha used (g)	Extrusion pressure (kg)	Tensile load at break (kg)	Elongation (%)
Powder of Example 11	10	3250	11.0	224
Powder of Example 13	20	2300	11.5	230

Example 14

- The same procedure as in Example 9 but using ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (2 g) in place of aluminium nitrate (0.06 g) and effecting addition of petroleum benzin at the stage II was repeated. Separation of glass fiber powder in the filtrate was not observed. The obtained powder colored slightly due to ferric ion.

Example 15

- The same procedure as in Example 9 but using magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (4 g) in place of aluminium nitrate (0.06 g) and effecting addition of petroleum benzin at the stage II was repeated. Separation of glass fiber powder in the filtrate was less than 5 g.

Example 16

- The same procedure as in Example 9 but using sodium laurylsulfate in place of ammonium perfluorooctanoate was repeated. Separation of glass fiber powder in the filtrate was less than 5 g.

"Petroleum benzin" as used herein may refer to "petroleum ether".

CLAIMS

1. A process for preparing a powder of a polymer of tetrafluoroethylene and a filler which is negatively charged in water, which comprises mixing, in the presence of an anionic surfactant and a water-immiscible organic liquid, an aqueous dispersion of particles of the polymer and an aqueous dispersion of positively charged particles of the filler having polyvalent cations adsorbed on the surfaces thereof, and recovering coagulated particles from the resultant dispersion.
2. A process according to claim 1, wherein the particles of the polymer in the aqueous dispersion thereof have an average particle size of from 0.1 to 0.3 μ .
3. A process according to claim 1 or claim 2, wherein the particles of the filler in the aqueous dispersion thereof have an average particle size of from 0.001 to 200 μ .
4. A process according to any preceding claim, wherein the volumetric ratio of the polymer particles to the filler particles is from 100:5 to 100:60.
5. A process according to any preceding claim, wherein the polyvalent cation is a polyvalent metal ion.
6. A process according to claim 5, wherein the polyvalent metal is aluminium, iron, magnesium, calcium, barium, copper or zinc.
7. A process according to any preceding claim, wherein the anionic surfactant is a fluorine-containing carboxylate or sulfonate.
8. A process according to any preceding claim, wherein the water-immiscible organic liquid has a boiling point of from 30 to 150°C and a surface tension of not more than 35 dyne/cm.
9. A process according to claim 1 substantially as described in any of the Examples.